

Standard molar enthalpy of formation of $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$

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Received 4 March 2004; received in revised form 8 May 2004; accepted 17 May 2004

Available online 26 November 2004

Abstract

The mixed complex of Nd^{3+} with glycine and alanine, $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, was synthesized and characterized by IR, elementary analysis, thermogravimetric analysis and chemical analysis, and the dissolution enthalpies of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$, $2\text{Gly}(\text{s}) + 3\text{Ala}(\text{s})$ and $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ were determined in 2 mol/L HCl by the classical solution calorimetry. By designing a thermochemical cycle according to Hess' law and through calculation, we obtained the reaction enthalpy of neodymium chloride six-hydrate with glycine and alanine: $\Delta_r H_m^\circ(298.15 \text{ K}) = 37.24 \pm 0.299 \text{ kJ/mol}$, and the standard enthalpy of formation of $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$: $\Delta_f H_m^\circ[\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}] = -4441.6 \pm 8.262 \text{ kJ/mol}$.

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Keywords: Neodymium chloride six-hydrate; Glycinee; Alanine; Thermochemistry; Standard molar enthalpy of formation

1. Introduction

Rare earth ions possess antibacterial and inflammation-diminishing function [1] and can be used in biochemistry as a probe of the calcium ion in organism. Moreover, amino acids are the structure unit of proteins and the complexes of rare earth ions with amino acids possess anti-tumour function [2]. So it is very interesting to make researches on the complexes, which has become a hotspot in the cross field of chemistry and biology in recent years [3–5]. It is necessary to obtain their basic thermodynamic data as the gist and basis for theoretical researches and industrial designing when they are synthesized and developed industrially. However, the thermodynamic properties of the complexes have not been reported yet. Therefore, with solution calorimetry on a new type of solution-reaction isoperibol calorimeter, we determined the dissolution enthalpies of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$, $2\text{Gly}(\text{s}) + 3\text{Ala}(\text{s})$ and $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ in 2 mol/L HCl. By designing a thermochemical cycles according to Hess' law, we obtained, through calculation, the molar enthalpy of the reaction: $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) + 2\text{Gly}(\text{s}) + 3\text{Ala}(\text{s}) = \text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{l})$ and

estimated the standard molar enthalpy of formation of $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$.

2. Experimental

2.1. Chemicals and instruments

$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ (obtained from Shanghai Reagent Company) used was of analytical reagent grade, a purity >99.5% and it was dried in a desiccator containing sulfuric acid of 60% [6] at room temperature to constant mass prior to use. Glycine (obtained from Tianjin Sanitary Material Factory) used was of biochemical reagent grade, a purity >99.0%. DL- α -Alanine (obtained from Shanghai Kangda Amino Acid Factory) used was of biochemical reagent grade, a purity >99.0%, KCl (obtained from Shanghai Reagent Factory), calorimetric primary standard of purity >99.99%, was dried in a vacuum oven for 6 h at 135 °C prior to the use.

Elemental analyzer (Perkin-Elmer 2400 CHN, USA), FT-IR spectrometer (Avatar 360, with KBr pellet, USA), thermogravimetry analyzer (Perkin-Elmer TG6, at a heating rate of 10 $\text{E}l/\text{min}$ in flowing N_2 , USA), Abbe refractometer (WAY, Shanghai, China), ultraviolet-visible spectrophotometer (U-3010, HITACHI, Japan), solution-reaction isoperibol calorimeter (SRC 100, Wuhan University, China).

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2.2. Synthesis and characterisation of the coordination compound

The synthesis and purification of $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ was carried out as previously described in literature [7]. A 16.1 mmol of crushed $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ was dissolved in 65 cm^3 of water, which was added into 45 cm^3 the water solution (pH 5) of 30 mmol of glycine and 45 mmol of DL- α -alanine. The reaction mixture was refluxed at $70\text{--}80^\circ\text{C}$ A for 2 h on magnetic stirring, and then evaporated to dryness and cooled to room temperature. When acetone was added into the cooling reaction mixture, the dope was separated out, and washed with absolute ethyl alcohol after the mother solution is raved about, and then the product was put into a desiccator containing calcium chloride and kept until the mass of the crystal became a constant. The chemical composition of the synthetic sample was determined by elemental analysis for C, H, and N, by EDTA titration for Nd^{3+} [8], by mercury salt titration for Cl^- and by difference and TG-DTG curve for H_2O . The analysis results proved that the composition of the complex was $\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ and its purity was $>99.56\%$.

2.3. The solution-reaction isoperibol calorimeter and calibration

The solution-reaction isoperibol calorimeter (SRC 100) consisted of a water thermostat, a pyrex-glass Dewar, a glass sample cell, a heater for calibration and equilibration purposes, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter and a personal computer for data acquisition and processing. The sample cell was a small glass cup. The heater and the thermistor were placed in two glass tubes separately, which were filled with silicone oil as a heat transfer medium. The Dewar vessel with an internal volume of 100 ml, equipped with a twin-blade stirrer inside and serving as a mixing chamber, was submerged in the water thermostat. The precisions of temperature control and temperature measurement were ± 0.001 and $\pm 0.0001 \text{ K}$, respectively. The principle and structure of the calorimeter are described in detail elsewhere [9].

The solution-reaction isoperibol calorimeter (SRC 100) was used for this study and the calibration of the calorimeter was tested by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.1000 mol/L HCl and KCl (calorimetric primary standard) in water at 298.15 K . The mean dissolution enthalpies were $-29,776 \pm 16 \text{ J/mol}$ for THAM and $17,597 \pm 17 \text{ J/mol}$ for KCl which are in conformity, respectively, with the published data ($-29,766 \pm 31.5 \text{ J/mol}$ for THAM [10] and $17,536 \pm 9 \text{ J/mol}$ for KCl [11]). The uncertainties of both are less than 0.5%. This shows that the device for measuring the enthalpy of solution used in this experiment is reliable.

2.4. Determination of dissolution enthalpies

The method of dissolution enthalpies determination for the samples is the same as for the calibration of the calorimeter with THAM and KCl . The temperature of the calorimetric experiment was 298.15 K . During each electrical energy calibration, the electrical current (I) was set at 10.0016 mA , and the resistance of the electrical heater was 1003.6Ω .

$\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ can be regarded as the product of the following reaction (1), and the thermochemical cycle was designed as Fig. 1.

The UV spectrums and refractive indexes of the final solution of the reactants and the final solution of the products can be used to determine whether they have the same thermodynamic state. In the present experiments, we determined the spectrum and refractive indexes of solution B and solution D in Fig. 1, and discovered the duplicate UV spectroscopy (Fig. 2) and equal refractive index ($n_{25^\circ\text{C}} = 1.3489$). It proves that both have same thermodynamics state and that the thermochemical cycle of the reaction (1) is reliable.

The chosen calorimetric solvent must dissolve the chemicals in the sample cell completely and very rapidly. So the choice of the calorimetric solvent is very important in the calorimetric experiments. Rigorous control of the stoichiometry was maintained through each series of experiments to ensure that the final solutions resulting from the dissolution of the reactants were of the same composition as those from the dissolution of the products. 2 mol/L HCl is the most appropriate solvent in the experiment.

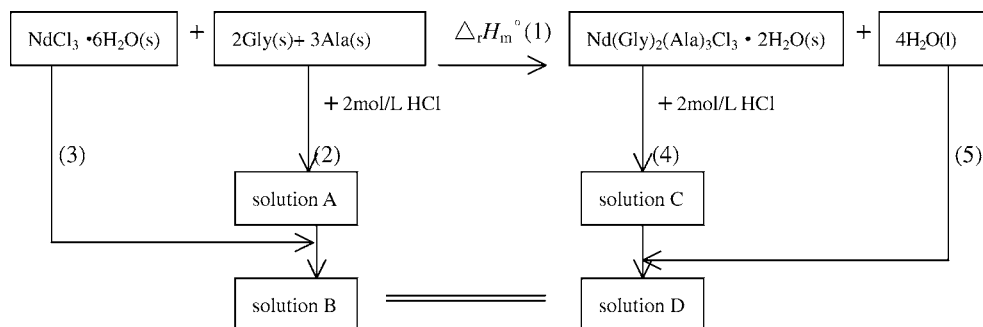


Fig. 1. Thermochemical cycle of the reaction (1).

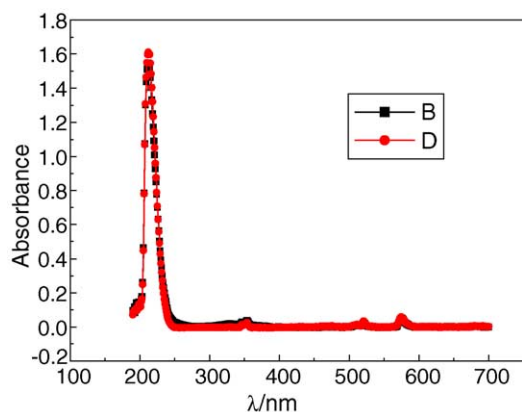
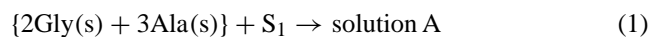


Fig. 2. UV spectrum of the final dissolution state of the reactants and products in 2 mol/L HCl.

The mixture of Gly(s) and Ala(s) ($n_{\text{Gly}}:n_{\text{Ala}} = 2:3$) was grinded in an agate mortar. The mixture (0.418 g) was placed into a sample cell in calorimeter and HCl (100 cm³, 2 mol/L) was added into the reaction vessel. Calorimeter was adjusted to a constant temperature and the dissolution enthalpy was determined. Five experimental series were performed:

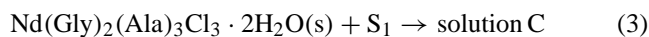


where S_1 was the calorimetric solvent (100 cm³ of 2.00 mol/L HCl).

The solution A above was kept in the reaction vessel. Powder NdCl₃·6H₂O (0.360 g) was put into the sample cell. Five experimental series were performed:



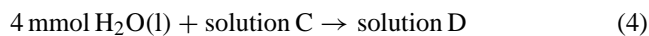
Powder Nd(Gly)₂(Ala)₃Cl₃·2H₂O (0.703 g) was put into the sample cell in calorimeter, and HCl (100 cm³, 2 mol/L) was put into the reaction vessel. Calorimeter was adjusted to a constant temperature. Five experimental series were performed:



where S_1 was the calorimetric solvent (100 cm³ of 2 mol/L HCl).

The calorimetric results of reactions (2)–(4) are listed in Table 1.

The solution C above was kept in the reaction vessel. 4 mmol H₂O(l) was added into the reaction vessel:



3. Results and discussion

3.1. Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1, in which m is the mass of the sample, t the heating period of electrical calibration, Q_s the heat effect, ΔE_s the voltage change during the sample dissolution, ΔE_e the voltage change during the electrical calibration and $\Delta_s H_m^\circ$ the molar enthalpy of solution of solute. The molar enthalpy of solution was finally calculated from the equation

$$\Delta_s H_m^\circ = \left(\frac{\Delta E_s}{E_e} \right) I^2 R t \left(\frac{M}{m} \right)$$

where R is the resistance of the heater, I the current, and M the molar mass.

Table 1
Dissolution enthalpies of [2Gly(s) + 3Ala(s)] [NdCl₃·6H₂O(s)] and [Nd(Gly)₂(Ala)₃Cl₃·2H₂O(s)] in 2 mol/L HCl at 298.15 K

System	No.	m (g)	ΔE_s (mV)	ΔE_e (mV)	t (s)	Q_s (J)	$\Delta_s H_m^\circ$ (kJ/mol)
2Gly(s) + 3Ala(s) in 2 mol/L HCl	1	0.4186	5.650	6.560	366.8	33.2449	33.142
	2	0.4181	5.820	6.00	342.0	33.040	32.249
	3	0.4188	5.610	6.120	355.0	33.2423	33.132
	4	0.4183	5.640	6.010	346.8	33.2490	33.168
	5	0.4183	5.690	6.140	356.6	33.2691	33.198
$\Delta_s H_m^\circ(2) = \Delta_s H_m^\circ[2\text{Gly(s)} + 3\text{Ala(s)}, 298.15 \text{ K}] = 33.178 \pm 0.042 \text{ kJ/mol}^a$							
NdCl ₃ ·6H ₂ O(s) in 2Gly·3Ala·2 mol/L HCl	1	0.3576	3.050	3.670	105.00	−8.7604	−8.786
	2	0.3612	2.890	2.720	81.45	−8.6880	−8.626
	3	0.3611	2.950	2.710	80.27	−8.7721	−8.712
	4	0.3607	2.890	2.540	75.98	−8.6789	−8.629
$\Delta_s H_m^\circ(3) = \Delta_s H_m^\circ[\text{NdCl}_3 \cdot 6\text{H}_2\text{O(s)}, 298.15 \text{ K}] = 8.690 \pm 0.265 \text{ kJ/mol}^a$							
Nd(Gly) ₂ (Ala) ₃ Cl ₃ ·2H ₂ O in 2 mol/L HCl	1	0.7021	4.380	4.140	119.9	−12.7368	−12.772
	2	0.7024	4.373	4.110	119.4	−12.7451	−12.775
	3	0.7032	4.360	4.310	125.4	−12.7352	−12.751
	4	0.7045	4.380	4.350	126.4	−12.7771	−12.769
	5	0.7054	4.360	4.260	123.8	−12.7203	−12.696
$\Delta_s H_m^\circ(4) = \Delta_s H_m^\circ[\text{Nd(Gly)}_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O(s)}, 298.15 \text{ K}] = -12.753 \pm 0.132 \text{ kJ/mol}^a$							

^a Uncertainty was estimated as twice the standard deviation of the mean of the results.

3.2. Treatment of $\Delta_d H_m^\circ$ for reaction (5)

The dilution enthalpy is -0.001 kJ/mol [6] when “ $4\text{H}_2\text{O}(l)$ ” is put into 2 mol/L HCl. And because of small concentration of Nd^{3+} , Cl^- , Gly and Ala in solution C, the dilution enthalpy of $[\text{Nd}^{3+} \cdot 2\text{Gly} \cdot 3\text{Ala} \cdot 3\text{Cl}^-]$ is small when “ $4\text{H}_2\text{O}(l)$ ” is put into the solution. The latter is much smaller than the former and can be neglected. So $\Delta_d H_m^\circ(5) = -0.001$ kJ/mol [6].

3.3. The molar enthalpy of reaction (1)

According to Hess' Law, the standard molar reaction enthalpy of the reaction (1) is obtained:

$$\begin{aligned} \Delta_f H_m^\circ[\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}] \\ = [37.24 - 4 \times (-285.830) + (-2874.4) + 2 \times (-528.5) + 3 \times (-563.6)] \\ \pm [\sqrt{(0.598)^2 + (4 \times 0.040)^2 + (8.0)^2 + (2 \times 0.4)^2 + (3 \times 0.6)^2}] = -4441.6 \pm 8.262 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\circ(1) &= \Delta_s H_m^\circ(2) + \Delta_s H_m^\circ(3) - \Delta_s H_m^\circ(4) \\ &\quad - \Delta_d H_m^\circ(5) = [33.178 + (-8.690) \\ &\quad - (-12.753) - (-0.001)] \\ &\quad \pm [\sqrt{0.042^2 + 0.265^2 + 0.132^2}] \\ &= 37.24 \pm 0.299 \text{ kJ/mol} \end{aligned}$$

3.4. Evaluation of $\Delta_f H_m^\circ[\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}(s)]$

According to thermodynamics principle, we know

$$\begin{aligned} \Delta_f H_m^\circ &= \Delta_f H_m^\circ[\text{Nd}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3 \cdot 2\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}] \\ &\quad + 4\Delta_f H_m^\circ[\text{H}_2\text{O}, l, 298.15 \text{ K}] \\ &\quad - \Delta_f H_m^\circ[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}] \\ &\quad - 2\Delta_f H_m^\circ[\text{Gly}, \text{s}, 298.15 \text{ K}] \\ &\quad - 3\Delta_f H_m^\circ[\text{Ala}, \text{s}, 298.15 \text{ K}]. \end{aligned}$$

According to [12]:

$$\Delta_f H_m^\circ[\text{H}_2\text{O}, l, 298.15 \text{ K}] = -285.830 \pm 0.040 \text{ kJ/mol}$$

According to [13]

$$\begin{aligned} \Delta_f H_m^\circ[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}] \\ = -2874.4 \pm 8.0 \text{ kJ/mol} \end{aligned}$$

According to [14]:

$$\begin{aligned} \Delta_f H_m^\circ[\text{Gly}, \text{s}, 298.15 \text{ K}] \\ = -528.5 \pm 0.4 \text{ kJ/mol.} \\ \Delta_f H_m^\circ[\text{DL-}\alpha\text{-Ala}, \text{s}, 298.15 \text{ K}] \\ = -563.6 \pm 0.6 \text{ kJ/mol} \end{aligned}$$

and the above-mentioned values:

$$\Delta_r H_m^\circ = 37.24 \pm 0.598 \text{ kJ/mol.}$$

So that

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